

How Atomic Clusters Change Their Structures between Icosahedron and fcc

— *Molecular Dynamics Simulation of LJ Particles* —

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Formation of free clusters and their structures are discussed with the molecular dynamics simulations. The evaporation process plays an important role to generate the magic number clusters and their structures. It was confirmed that the different structure clusters are formed even from the same size liquid clusters after evaporation. The difference is only the first configuration of the liquid clusters.

§1. Introduction

Structure change in atomic clusters may be a function of energy difference among the possible structures and the kinetics to which the structures change. Much attention was focussed on the energy difference of the cluster in the theoretical calculations using Lennard-Jones (LJ), metal and some other molecular potentials. We have been approaching this problem from the kinetic point of view using molecular dynamics with the LJ potentials.^{1) - 6)}

$$U_{ij} = 4\epsilon \left\{ \left(\frac{r_{ij}}{\sigma} \right)^{-12} - \left(\frac{r_{ij}}{\sigma} \right)^{-6} \right\} \quad (1.1)$$

LJ potentials are representative of the interactions in the rare gas atom clusters and others connected by the van der Waals interaction.

Rare gas clusters are experimentally generated by the supersonic expansion technique, in which the rare gas is expanded into a vacuum chamber from a small nozzle. Atoms hit another atoms to the one direction to make velocities of all atoms be the same value. A supersonic wave is generated. When we look at atoms from an atom in the jet, all atoms look to stop even though the absolute velocities of atoms are high. Thus, the atoms aggregate because of the low thermodynamic temperature. In order to avoid clusters growing so much, a part of the jet is introduced to another high-vacuum chamber. The distance from the nozzle, the nozzle diameter, and the first pressure affect on the cluster sizes and their distributions. The formed clusters are detected by a mass spectrometer after ionization. The observed mass spectra are generally not uniform, giving some high peaks at the certain numbers which are called magic numbers. In case of rare gas clusters, observed magic numbers, 13, 55, 147, ..., are corresponding to the series of number of atoms, N_{magic} ,

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$$N_{\text{magic}} = 1 + \sum_k (10k^2 + 2), \quad k = 1, 2, 3, \dots, \quad (1.2)$$

when atoms are built up layer by layer on an icosahedron (Ih) as shown in Fig. 1(a). Some other series of numbers due to poly-icosahedral and partially closed Ih clusters are also observed. These typical magic number peaks are observed for Xe and Kr clusters and for very large Ar clusters.⁷⁾ Since small argon clusters are generated from the stable core, Ar²⁺, the different magic numbers are observed.

Although the measurement of X-ray diffraction from clusters would give the good information about the structures of the clusters, the X-ray diffraction is so weak to be used. The electron diffraction was, instead, measured by Torchet et al. by focusing an electron beam to the supersonic jet.⁸⁾ They found the structure change from Ih to fcc (face centered cubic) crystal structure around $N = 750$ with increase of the cluster size, where N is number of atoms in a cluster. A cuboctahedral fcc clusters are shown in Fig. 1(b).

The structure change is because of that icosahedral clusters have the five-fold symmetry which cannot exist in bulk states. Both Ih and cuboctahedral fcc clusters grow layer by layer (i.e. shell structure), giving the same series of magic numbers in Eq. (1.2). Although an icosahedron (13 atoms) has the same size of 20 triangles on the surface, the distance from the center to the top atoms are slightly shorter than the distance between the top atoms. Therefore, the stress in the cluster increases when layers are added on the surface. An ideal 13-atom fcc cluster has triangle and square facets on the surface with the same distance between atoms. No stress increases when layers are added to the surface. Details about Ih and fcc clusters are explained in Ref. 9). The transition size from Ih to cuboctahedral fcc clusters were estimated at $N = 10,000$ from calculation of the smaller clusters in the perfect structures,¹⁰⁾ where geometries were relaxed, i.e. at 0 K. This structure transition could be reconfirmed by the re-calculation of the clusters including the larger size

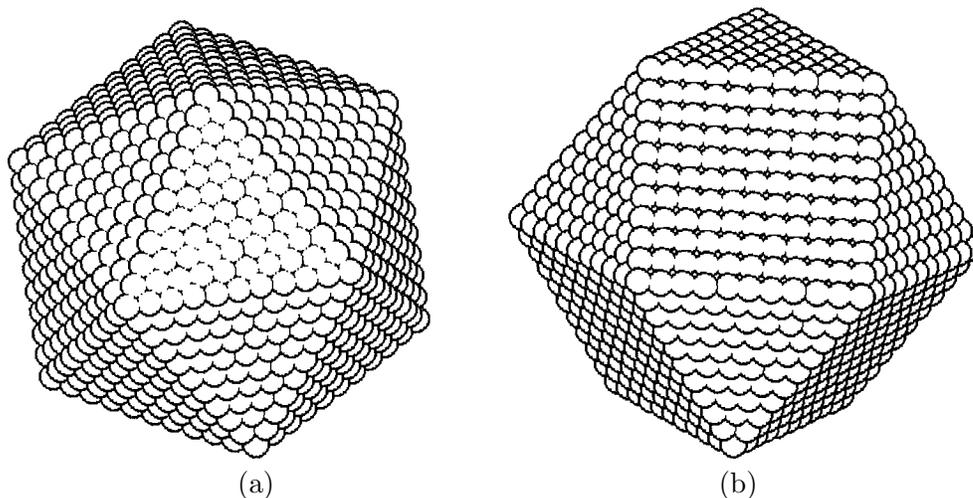


Fig. 1. Perfect (a) Icosahedral and (b) cuboctahedral fcc clusters of 3871 atoms.

using the LJ potential with no cutoff.¹¹⁾ The discrepancy between the transition sizes in the experiments and calculations could be explained assuming decahedral clusters. Mark's decahedral clusters (Dh) have the lower energy and the similar diffraction pattern as twin-fault fcc clusters.⁸⁾ The transition from Ih to Dh was estimated at $N = 1600$.⁸⁾

Calculations presented so far have been about perfect clusters of which atom numbers are discrete, though the various size clusters including imperfect clusters are experimentally formed. Another important difference of most of the calculation conditions from the experimental ones is temperature. Though it is difficult to measure the temperature of clusters, they are not at 0 K and are believed to be around 35 K in case of rare gas clusters produced by the supersonic expansion. It is necessary to consider these two points, imperfect structures and finite temperature, to analyze the cluster structure transition. Another important point is to consider the formation processes. Clusters are solidified (more correctly "are changed to a solid-like state"), when they are cooled. It is like a liquid-to-solid transition. Temperature decrease is attained by evaporation in case of Argon clusters. The importance of the evaporation process to produce the magic number clusters and their structures has been already presented for small clusters.^{2),3)}

In this note, we will show the results of md simulation for the formation of large clusters ($N = 1000 - 2000$). The liquid clusters, which were prepared by cooling the LJ vapor under the periodic boundary condition, did not change their structures to the same unique kind even starting from the same size but they changed to either fcc or icosahedral clusters. The difference in the conditions was only the initial value of the random generator used to prepare the liquid droplets.

§2. Results and discussion

Figure 2 shows two kinds of typical outer shapes of the solid clusters after evaporation from the same size liquid droplets of $N = 1920$. The structures are based

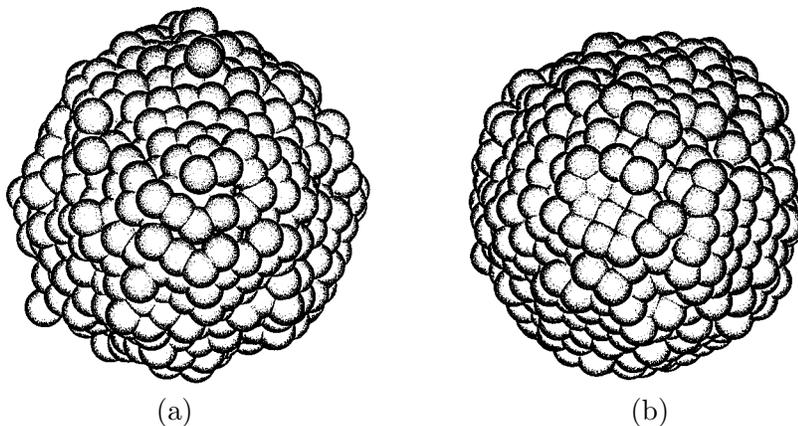


Fig. 2. Outer shapes of the solid clusters after evaporation from the liquid droplets of $N = 1920$. (a) icosahedral cluster, (b) fcc cluster.

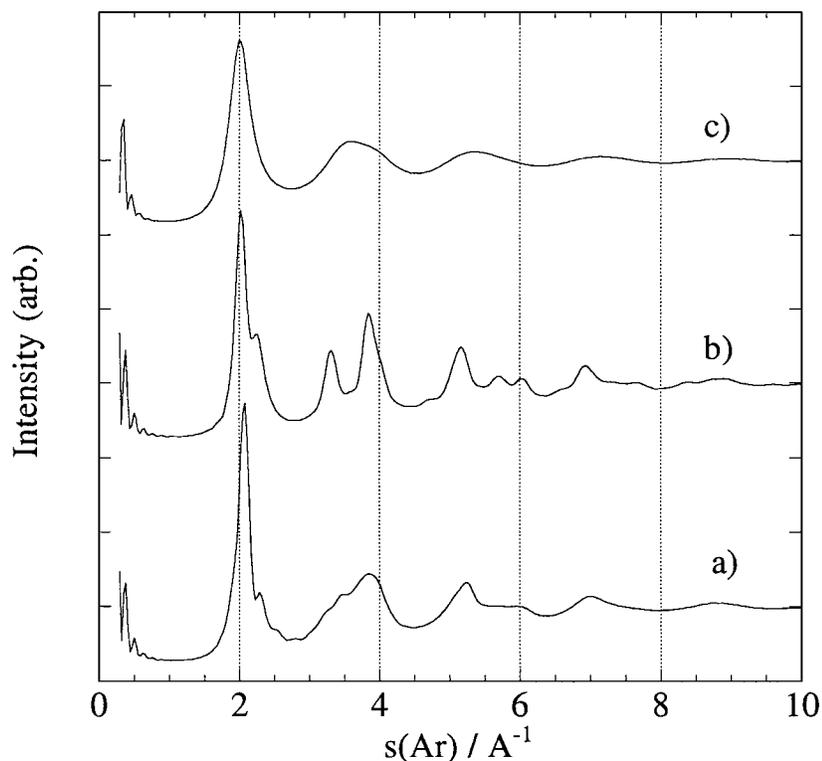


Fig. 3. Structure factors of (a) icosahedral and (b) fcc clusters formed from (c) liquid droplet of $N = 1920$.

on (a) icosahedron and (b) cuboctahedron (fcc). The structures can be determined by the shapes and the structure factors shown in Fig. 3. Fcc clusters gave the (100) and (111) faces but icosahedral ones showed only the (111)-like face. Atoms are ordered on several planes in fcc clusters, and those in Ih clusters are in the ten-fold symmetry. Structure factors of the pure fcc cluster show the first peak splitting, though the calculated structure factor of the fcc clusters formed by evaporation did not give the complete split as can be seen in Fig. 3(b). This unsplitting is because of the twin faults in the clusters.¹²⁾

Since clusters are the finite number of atoms system, their structures are not uniquely defined at a finite temperature. This may be the main reason of the generation of the different structures from the same conditions, but a kinetic effect is another possibility to have two different structures.

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